Synthesis of Core–Shell Type Microsphere with Reactive Seed Microspheres

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ABSTRACT: Monodispersed poly(methyl methacrylate) (PMMA) particles (seed microspheres) were synthesized with the living radical initiators, tetramethylthiuram disulfide, or *p*-xylene dimethyldithiocarbamate by suspension polymerization in water media with and without divinyl benzene as a crosslinker. Monodispersed spherical microspheres with PMMA core–polyacrylamide shells were synthesized by UV irradiation to the seed microsphere–acrylamide aqueous solution. The content and the molecular weight of the polyacrylamide shell chain were controlled by changing the acrylamide feed and irradiation time of the UV light. The microspheres became dispersible to water after the UV irradiation. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 211–216, 1998

Key words: core–shell type microsphere; living radical polymerization; suspension polymerization; polystyrene; polyacrylamide

INTRODUCTION

Synthesis of core–shell type polymer microspheres has been well investigated. We studied the synthesis of core–shell type polymer microspheres upon crosslinking of the spherical domains of the microphase separation of block and graft copolymerization.[1–5] Each core–shell type microsphere synthesized by our method was composed of a crosslinked core and many shell chains with one end attached to the surface of core and the other end free. This structure is very similar to that of $(AB)n$ type star block copolymers with many arms that were proposed by Witten et al.[6] De la Cruz and Sanchez[7] proposed the super lattice formation of the $(AB)n$ type star block copolymers in solvent due to their structural peculiarity.

Due to the structural similarity of the core–shell type polymer microspheres to the $(AB)n$ type star block copolymers, the superlattice formation of the core–shell type microspheres was also expected. In fact, the super lattice formations of the core–shell type microspheres with body centered cubic (bcc) and face centered cubic (fcc) structures were found for poly(2-vinyl pyridine) or poly(4-vinyl pyridine) core–polystyrene shell type polystyrene microspheres in a good solvent and the solid state. By further investigation, the super lattice structures could be hierarchically controlled from bcc to fcc via a bcc–fcc mixture state.[8–10] To obtain monodispersed microspheres, all material block copolymers were synthesized by an anionic living polymerization technique. However, it is well known that anionic living polymerization has many disadvantages, such as technical difficulty, requirements for well-purified materials, and so forth.

On the other hand, radical living polymerization was investigated because of its convenience and good molecular weight control.[11] The most interesting feature of the living radical polymerization is the transfers to the propagation end of the chain, instead of the initiators of the usual radical polymerization existing at the initiated end of the chain. Therefore, it is useful to produce block copolymers.

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If seed microspheres are synthesized with the radical living initiator (iniferter) by suspension polymerization, a secondary monomer will be grafted onto the seed microspheres by using the iniferter group in the microspheres. When the seed microspheres do not absorb the secondary monomer, grafting will start on the surface of the seed microspheres, not in the seed microspheres. This suggests that the core–shell type polymer microspheres will be synthesized by using this method. Because the grafting is propagated livingly, the molecular weights of the shell chains of the secondary monomer will be easily controlled. Additionally, the iniferter groups introduced into the polymer are straggable.[11] Thus, these seed microspheres will be easy to handle.

The main purposes of this article were to synthesize the reactive seed microspheres with the iniferter and to graft the secondary monomers onto the seed microspheres. For these purposes, methylmethacrylate (MMA) and acrylamide (AAm) were chosen as the seed and secondary monomers. As the radical living initiators, tetramethylthiuram disulfide (TMTD) and *p*-xylene dimethyldithiocarbamate (*p*-XDC) were used. The AAm monomer is soluble in water and does not absorb into the poly(methyl methacrylate) (PMMA). To make the properties of the seed microspheres clear, the PMMA seed microspheres with and without crosslinking with divinylbenzene (DVB) were obtained. The molecular weights of the PMMA chains in the seed microspheres were measured by gel permeation chromatography (GPC). Shape and size of the microspheres were estimated by scanning electron microscopy (SEM) and dynamic light scattering (DLS).

EXPERIMENTAL

Synthesis of Seed Microspheres

For purification, MMA and DVB were distilled under a vacuum. AAm was re-crystallized from chloroform. MMA, solvent, and TMTD or *p*-XDC[12] were sealed into glass ampoules under nitrogen. The ingredients of the systems are shown in Table I. The ampoule was shaken at 150 rpm at 78°C for 8 h. After reaction, the products were precipitated in excess methanol, separated by a centrifuge at 3500 rpm for 10 min, and collected. The collected products were dried under a vacuum at room temperature. The products were stored in the dark at 0°C.

Grafting of AAm onto Seed

The seed microsphere (0.1 g), 10 mL of water, and the AAm were sealed into a Pyrex ampoule under a vacuum. The feed is listed in Table II. The solution was exposed to light for a certain time at room temperature using a high voltage mercury lamp (300 W, 100 V) without wavelength control. The products were precipitated into excess methanol, washed with methanol, collected, and dried under a vacuum at room temperature.

Characteristics

Morphological Observation

For shape observation of the products, the reacted solution was cast on the glass, dried quickly, and platinum was sputtered with an ion sputterer (Hitachi E-1010). The samples were observed with a scanning electron microscope (JEOL T-220) at 15 kV.

DLS

To determine the size of the products in the solution, the hydrodynamic radii of the products in the solution were measured with a DLS (Photal DLS-7000) at 20°C at an angle of 90°.

Molecular Weight Measurement

Esterification and GPC Measurements. The weight-average molecular weight (M_w) and the distribution of the molecular weight (M_w/M_n) of PMMA chains in the seed microspheres without crosslinking were estimated by combining the GPC data (Tosoh HPLC-8020, GPC with THF as an eluent at 38°C, a TSK-gel GMHXL column, and a flow rate of 1.0 mL/min) and intrinsic viscosities in THF at 38°C by using a universal calibration method. To measure the number-average molecular weight (M_n) of the polyacrylamide (PAAm) grafted onto the PMMA sphere, the pAAm was converted to polymethyl acrylate (PMA) measured with the GPC. The degree of esterification and PAAm contents were measured with an FTIR spectrophotometer (Shimadzu DR-8010).

Turbidimetric Behavior

Sample polymer (0.05 g) was dissolved in 20 mL of water, and then methanol was added stepwise with vigorous stirring in a cell at 25°C. At each step the turbidity of the solution was measured with a digital multimeter (TDA DMM-9152) with

Table I Ingredients and Results of PMMA Core Synthesis

Sample Name	Ethanol Content	Initiator[a]	DVB[b] Concn	D_n[c] (μm)	D_w/D_n[c]	M_n[d] $\times 10^{-4}$	Chain[e] Number
A0	0	TMTD	0	1.42	1.28	1.71	3.2×10^7
B0	0	TMTD	8.7×10^{-3}	1.50	1.16	—	—
A20	20	TMTD	0	0.37	1.09	1.85	1087
B20	20	TMTD	8.7×10^{-3}	0.56	1.12	—	—
A30	30	TMTD	0	0.53	1.01	1.72	3234
B30	30	TMTD	8.7×10^{-3}	0.89	1.01	—	—
A40	40	*p*-XDC	0	0.49		3.44	1331

General condition: [MMA] = 0.87 mol/L.
[a] TMTD, 1 wt % to monomer; *p*-XDC, 1.8 wt % to monomer.
[b] Divinyl benzene concentration.
[c] D_n and D_w are the number-average and weight-average diameters, respectively, determined by SEM.
[d] Number-average molecular weight of PMMA chain determined by GPC.
[e] Chain number of PMMA in a microsphere.

a dc power supply (NOSIC MSA18-1) without wavelength control.

RESULTS AND DISCUSSION

Synthesis of PMMA Seed Microspheres

First the suspension polymerization was carried out to synthesize the PMMA seed microspheres. Ingredients for the polymerization and results are listed in Table I. Figure 1 shows the typical micrograph of PMMA seed A20 observed by SEM. The products were found to be spherical with a narrow size distribution.

The increase of the ethanol fraction in the media up to 20 vol % led to the drastic decrease of the particle size. Over 20 vol %, however, the particle size increased slightly. Especially, at 30 vol %, the size of the PMMA microspheres synthesized with DVB clearly increased more than without DVB. This would be due to the fact that the DVB caused intersphere crosslinking during the suspension polymerization. The yield of PMMA microspheres of this study was less than 25%, even though the polymerization was carried out over 8 h. This was because the reaction temperature was too low for polymerization. However, as confirmed from the SEM observation, spherical microspheres with narrow size distributions could be obtained by suspension polymerization of MMA with the living radical initiators.

Grafting of AAm Monomers onto Seed Microspheres

Next the AAm was grafted onto the PMMA seed microspheres by using the remaining inifeter groups in the seed and UV light irradiation. The ingredients of grafting are listed in Table II. For all cases, the PMMA seed microspheres (white powder) were hardly dispersed in the water before the irradiation. After the UV light irradiation, however, the gross polymer solution turned clear and all products were dispersed into the water, in

Table II Conditions and Results of Graft Copolymerization of AAm onto PMMA Seeds

Sample Name[a]	Irradiation Time (h)	Feed AAm to MMA Unit (mol/mol)	Grafted AAm to MMA Unit (mol/mol)	D_n[c] (nm)	D_w/D_n[c]
A20-1	1.0	5.0	1.1	582	1.04
A30-1	1.5	3.5	1.4	468	1.03
A40-1	1.0	5.0	0.6	741	1.04
A40-2	1.5	5.0	2.4	953	1.04

[a] Sample name A20-1 indicates the microsphere synthesized with the A20 seed.
[b] Measured by FTIR.
[c] D_n and D_w are the number-average and weight-average diameters, respectively, determined by TEM.

spite of the fact that the PMMA was insoluble in water. This solubility change of the products suggests that the PAAm was grafted onto the PMMA spheres. However, there is no evidence that all PAAm chains were on the PMMA spheres. In other words, PAAm homopolymer was synthesized during grafting. To investigate the presence of the PAAm homopolymers in the gross polymer solution, the turbidimetric titration for the gross polymer of A20-1 was carried out in a water–methanol system.

Figure 2 shows the turbidimetric curves of the gross polymer solution and the PAAm homopolymer measured in the water–methanol system. The PAAm homopolymer was found to be precipitated in the 20 vol % methanol solution. For the gross polymer solution, the turbidity dropped twice at 17 and 20 vol % of the methanol fraction. The methanol fraction at the second decreasing of the gross polymer solution was exactly the same as that for the PAAm homopolymer. This clearly indicates that not only the grafted products but also the PAAm homopolymers were formed in the system by the UV light irradiation.

Two causes are proposed for the synthesis of the PAAm homopolymer during the grafting. One is the TMTD remaining in the PMMA seed microspheres and another is the chain transfer of radicals. For clarifying these, the PMMA seed microspheres were repurified with excess hexane and reacted with the AAm monomer again. The turbidimetric curve of the gross polymer solution of the repurified PMMA microspheres is shown in Figure 2(c). For this solution, the products precipitated at once at 17 vol % of the methanol fraction and PAAm homopolymer did not exist in the system. Moreover, the methanol volume fractions of the first drop in Figure 2(a) and 2(c) agreed quite well. Thus, it was concluded that the AAm was only grafted onto PMMA spheres when the PMMA seed microspheres were well purified. The well-purified PMMA seed microspheres were used for other grafting.

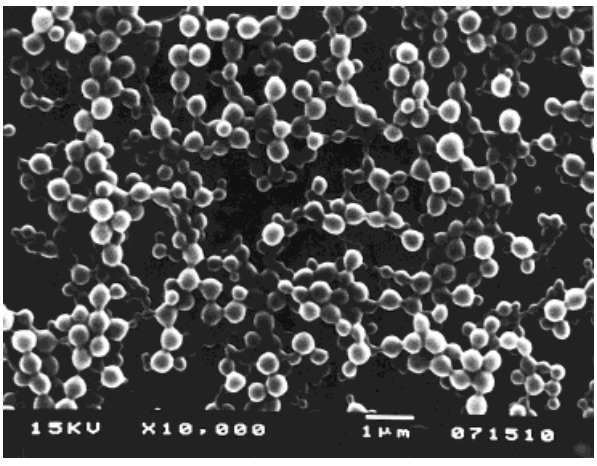

Figure 1 The SEM micrograph of Sample A20.

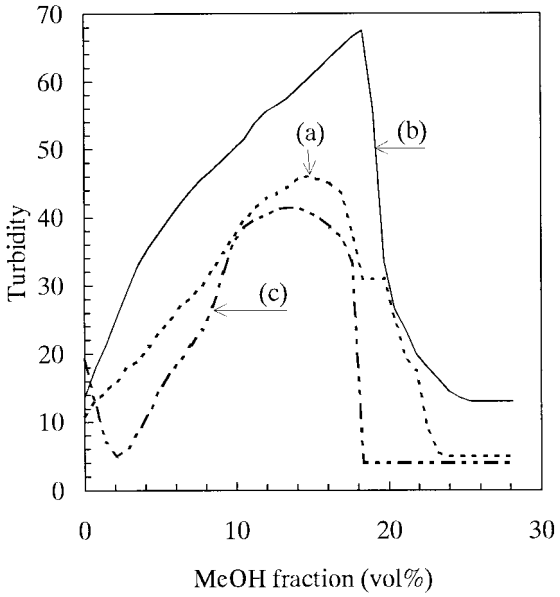

Figure 2 The turbidimetric titration curves of the A20 series: (a) the gross polymer, (b) PAAm homopolymer, and (c) gross polymer synthesized with the repurified A20.

Next, to investigate the change of structural properties, the SEM and transmission EM (TEM) observations were carried out. Figure 3 shows the SEM micrographs of A40-1 before and after the grafting. It is clearly observed that the diameter of A20 increased from 630 to 740 nm by grafting without changing the shape (spherical) and the diameter distribution index. Figure 4 shows the TEM micrograph of the cross section of A40-1 obtained by a microtome technique. The dark and white regions are the PAAm-rich area selectively stained with OsO_4 and the PMMA-rich area, respectively. From this micrograph, the PMMA core–PAAm shell structure of the microsphere was confirmed. The large disperity of diameter observed on the TEM micrograph resulted from the random slicing of the microspheres. Here it should be noted that the shell thickness was almost constant for any microsphere and the maximum diameter of the PMMA-rich area in grafted products estimated by TEM (650 nm) agreed well with the diameters of the PMMA seed observed

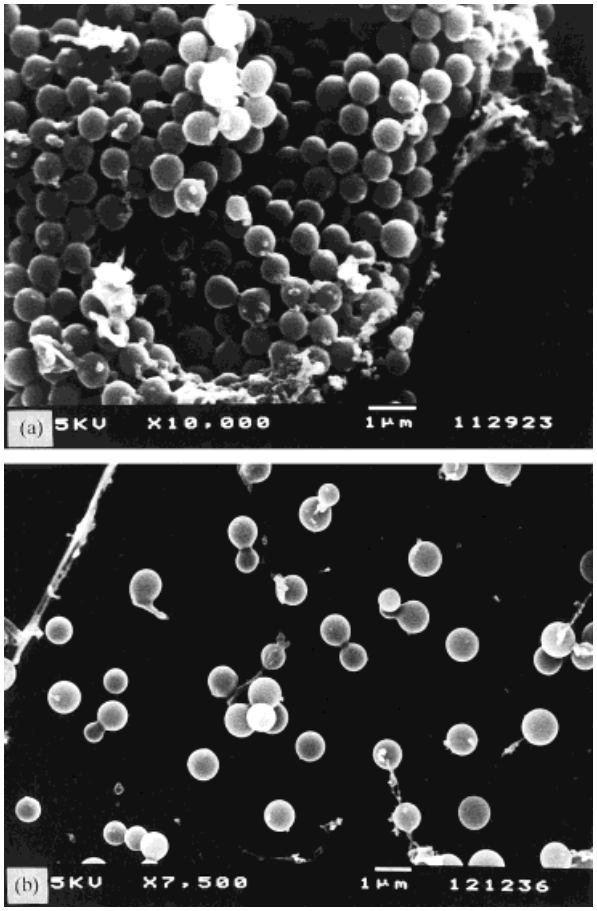

Figure 3 The SEM micrographs of the A40 series: (a) the PMMA seed A40 and (b) grafted product A40-1.

by SEM (630 nm). Therefore, AAm was found to be grafted onto the near surface of the PMMA seed microspheres without disturbing the spherical shape of the microspheres.

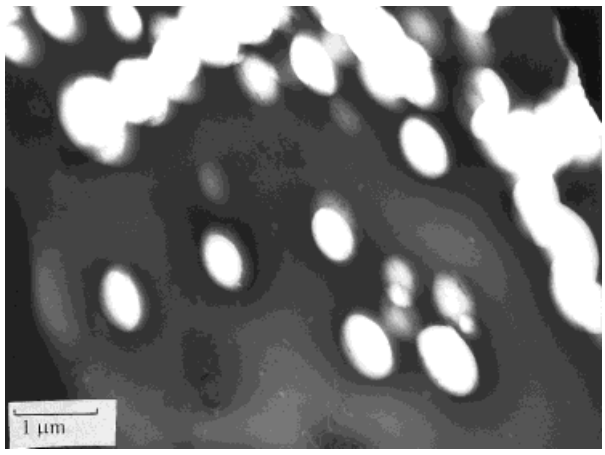

Figure 4 The TEM micrograph of the cross section of A40-1 selectively stained with OsO_4.

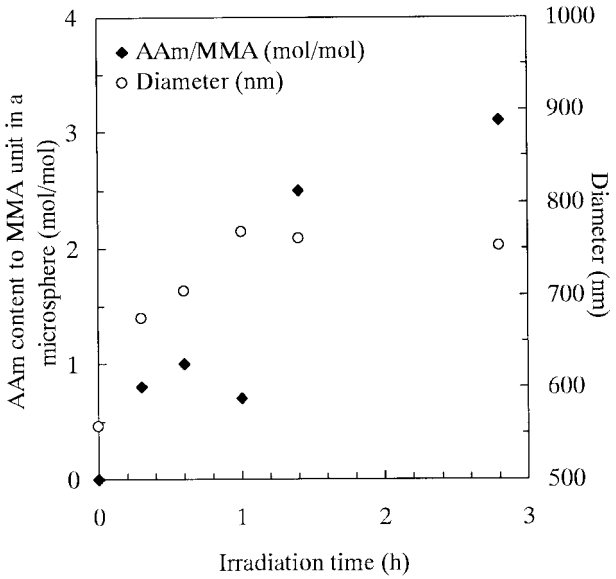

Figure 5 Effects of irradiation time on the AAm content and the diameter of the microspheres (B20 series).

Effects of Irradiation Time and AAm Feed on Characteristics of Microspheres

Figure 5 shows the time dependence on the grafted amount of AAm and the diameter of the products of the B20 series. Here the molar ratio of the AAm feed was set to 5.0 times the MMA units. The amount of grafted AAm in the products was linearly increased up to 1.5 h. Over 1.5 h the grafted AAm amount and the particle diameter were saturated. The maximum total yield of AAm monomer was 62 mol % in this system. Thus, this saturation suggests that the radical reaction did not livingly proceed in the later stage. However, it can be concluded that the amount of AAm was controllable by changing the irradiation time up to 1.5 h. For a detailed investigation of the radical polymerization in this system, the PAAm was esterified and the molecular weights of the products were measured by GPC. For all cases, the molecular weight of the products clearly increased as compared to that of the PMMA chain in the original seed microspheres. However, the polymerization behavior of the reactive end groups could not be estimated because all polymers could not be recovered after the esterification.

Figure 6 demonstrates the dependence of the feed amount of AAm on the grafted amount of AAm of the B31 series. The irradiation time was set to the saturated time of 1.5 h obtained from above. The grafted amount of AAm linearly increased with the increase of the feed amount of

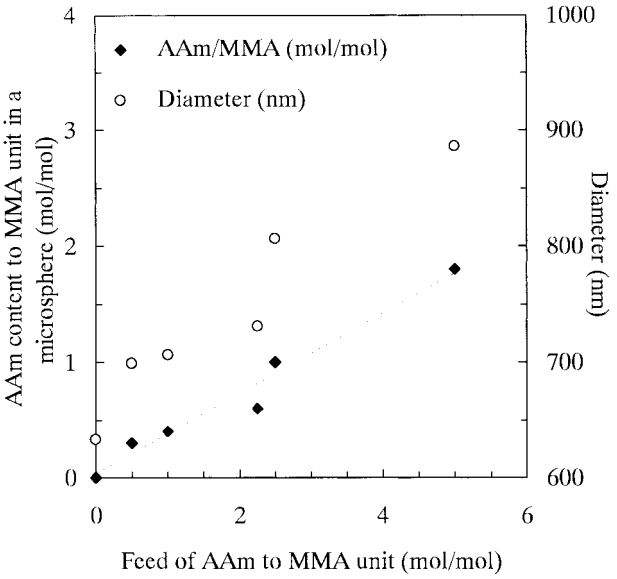

Figure 6 Effects of feed amount of AAm on the AAm content and the diameter of the microspheres (B30 series).

AAm. In this case, the saturation of the grafted amount of AAm could not be observed. Thus, the changing of the AAm feed was better for the control of the AAm content in the microspheres.

CONCLUSIONS

The PMMA seed microspheres were prepared with the living radical initiators TMTD or *p*-XDC with dispersion polymerization in water media. The diameters of the seed microspheres with narrow size distribution were changed by varying the ethanol content in the media. Then the secondary monomer, AAm, was grafted onto the PMMA seed microspheres in water by UV light irradiation. From SEM and TEM observations, the AAm was found to be grafted near the surface of the PMMA seed microspheres without disturbing their narrow size distribution. As a result, the core–shell structure of the microspheres was clearly confirmed. The PAAm content could be increased by increasing the irradiation time of the UV light and the feed of the AAm monomer. However, to avoid the side reactions, the control of the feed amount of AAm was concluded to be the better method for the control of the AAm content.

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